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**An optical–optical double resonance study of the perturbed O<sub>2</sub> d<sup>3</sup>sσg(1Πg) Rydberg state excited via single rotational levels of the b(1Σg<sup>+</sup>) valence state**

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# An optical–optical double resonance study of the perturbed $O_2$ $d3s\sigma_g(^1\Pi_g)$ Rydberg state excited *via* single rotational levels of the $b(^1\Sigma_g^+)$ valence state

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The perturbed  $v=3$  level of the  $d3s\sigma_g(^1\Pi_g)$  Rydberg state of  $O_2$  has been excited in an optical–optical double resonance (OODR) experiment *via*  $J=0-16$  of  $v=0$  of the  $b(^1\Sigma_g^+)$  state. The  $d(^1\Pi_g)$  state resonances were detected by ionization with one further probe photon near 340 nm. The range of  $J$  levels of the  $d(^1\Pi_g)$  state now accessed reveals a lack of variation in line widths that is not predicted by previous models of state-dependent predissociation. Instead, intensities of rotational lines in the ionization spectrum appear to be controlled by a  $J$ -dependent mixing of the  $d(^1\Pi_g)$  state with a nearby valence state that has a much lower ionization cross section at the probe wavelengths used. © 2000 American Institute of Physics. [S0021-9606(00)01730-X]

## I. INTRODUCTION

Several experimental studies of the first four vibrational levels of the  $d3s\sigma_g(^1\Pi_g)$  state of  $O_2$  by (2+1) resonance enhanced multiphoton ionization (REMPI) spectroscopy have been reported,<sup>1–4</sup> where the molecule was excited directly from both the  $X(^3\Sigma_g^-)$  ground state and the  $a(^1\Delta_g)$  valence state. These studies revealed many regions of significant perturbation, reflected in irregular band contours and varying rotational line widths, caused by interactions with a spectroscopically dark valence state. The primary interaction is with the  $I(^1\Pi_g)$  valence state, which is bound in the energy region of the crossing with the  $d(^1\Pi_g)$  state but which has a much larger equilibrium bond length. The arrangement of the potential energy curves is shown in Fig. 1. The crossing of the  $d(^1\Pi_g)$  and  $I(^1\Pi_g)$  states occurs between the  $v=2$  and  $v=3$  levels of the Rydberg state which are observed to be perturbed most strongly. All the perturbed rotational levels were broadened (no unperturbed levels were observed) and it was concluded<sup>5,6</sup> that a repulsive state, the  $I(^1\Pi_g)$ , crosses the  $I(^1\Pi_g)$ , to which it is weakly coupled.

An obvious, but hitherto unused starting state for accessing the  $d(^1\Pi_g)$  state is the valence  $b(^1\Sigma_g^+)$  state, which has the advantage over the ground state of being a singlet state. During a recent investigation of the photolysis of ozone,<sup>7</sup> we produced a significant yield of  $O_2$  in the  $b(^1\Sigma_g^+)$  state which was subsequently detected by resonant ionization using perturbed levels of the  $d(^1\Pi_g)$  state as intermediate states. Although the observed ion signals were strong, it was not possible to derive any information about the rotational distribution of the photofragments because of the perturbed

nature of the intermediate Rydberg state. Although the perturbations were an unwanted complication in identifying the nascent  $J$  state distribution of the  $b(^1\Sigma_g^+)$  state, the strength of the  $d\leftarrow b$  transition was clear.

In the present work, the  $v=3$  level of the Rydberg state was probed in a *rotationally selective* optical–optical double resonance (OODR) experiment in which *single* rotational levels of the  $b(^1\Sigma_g^+)$  state were first populated by direct optical pumping from the  $X(^3\Sigma_g^-)$  ground state. The  $d(^1\Pi_g)$  state was then excited from these rotational levels by coherent two-photon absorption and detected by ionization following absorption of a further photon as illustrated in Fig. 1. Although the  $b\leftarrow X$  transition is strictly forbidden on both parity and spin grounds, the transition does have a very weak magnetic dipole oscillator strength and can be pumped efficiently with a high power Ti:sapphire laser. The limited number of  $J$  levels accessed in the  $d(^1\Pi_g)$  state was controlled by the two-photon selection rules and allowed their absolute assignment. Simultaneous calibration of the probe laser allowed accurate determination of the transition energies.

## II. EXPERIMENT

The experimental arrangement is shown in Fig. 2. The (0,0) band of the  $b\leftarrow X$  transition of  $O_2$ , around 760 nm, was pumped by a Solar Laser Systems (LX 351) Ti:sapphire laser pumped by the second harmonic of a Solar Laser Systems (LQ 514) Nd:YAG laser. The narrow spectral line width ( $0.4\text{ cm}^{-1}$ ) output was generated using a combination of a prism beam expander and a holographic grating wavelength selector. The laser produced 25 mJ pulses of 8–9 ns duration at a repetition rate of 5 Hz. An excimer laser (Lambda Physik EMG201MSC) pumped dye laser (Lambda Physik FL2002), operating around 340 nm with the dye PTP, probed the re-

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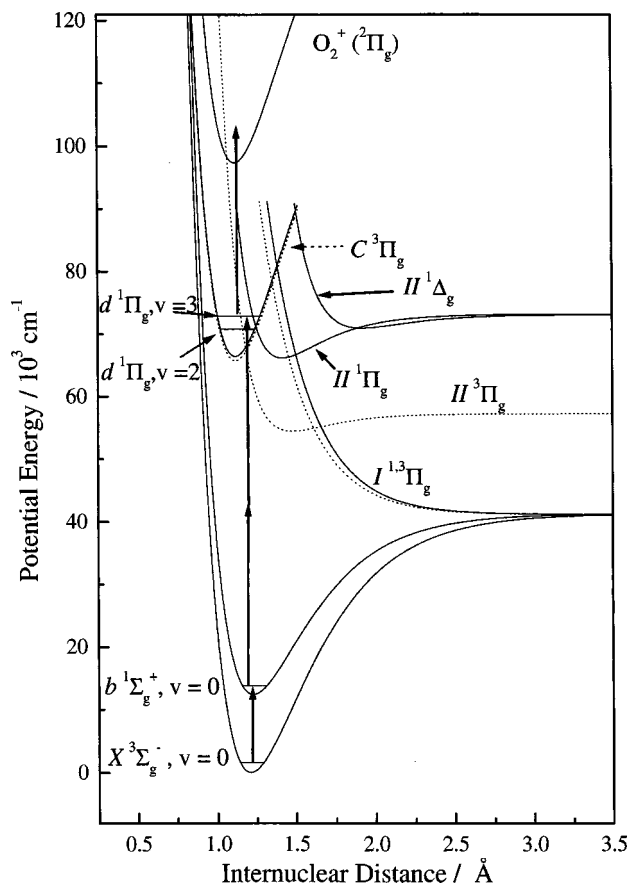


FIG. 1. The diabatic potential energy curves of some *gerade* electronic states of O<sub>2</sub> where the solid and dashed curves illustrate excited singlet and triplet states, respectively. The OODR pathway, followed by excitation of low vibrational levels of O<sub>2</sub><sup>+</sup>, is also shown.

sultant  $b(^1\Sigma_g^+, v=0, J)$  levels *via* a two-photon transition to  $v=3$  of the  $d(^1\Pi_g)$  state. The laser outputs were synchronized using a four-channel Stanford Research digital delay generator (DG 535) which produces pulses which are capable of externally triggering the flashlamps and *Q*-switch of the Nd:YAG laser as shown in Fig. 2. About 10% of each laser beam was directed onto a photodiode and the output fed to an oscilloscope in order to monitor their temporal overlap. Typically, a delay of 50–100 ns between the pump and probe lasers was used for maximum ion signal. The wavelength of the probe laser was calibrated by simultaneously recording the neon optogalvanic and ion spectra and the two-photon energy is estimated to be accurate to  $\pm 0.5$  cm<sup>-1</sup>.

The counter propagating pump and probe laser beams were focussed to an overlapping point in a differentially pumped ionization chamber using lenses of focal length 6 cm and intersected, at 90°, the pulsed molecular beam generated using a backing pressure of 600 torr of O<sub>2</sub>. The resulting ions were collected by a linear time-of-flight (TOF) mass spectrometer and the ion current from the microchannel plate (MCP) detector was processed by a boxcar integrator and stored on a PC.

### III. RESULTS

The rotational structure of a one-photon magnetic dipole transition between  $^3\Sigma_g^-$  and  $^1\Sigma_g^+$  states consists of four

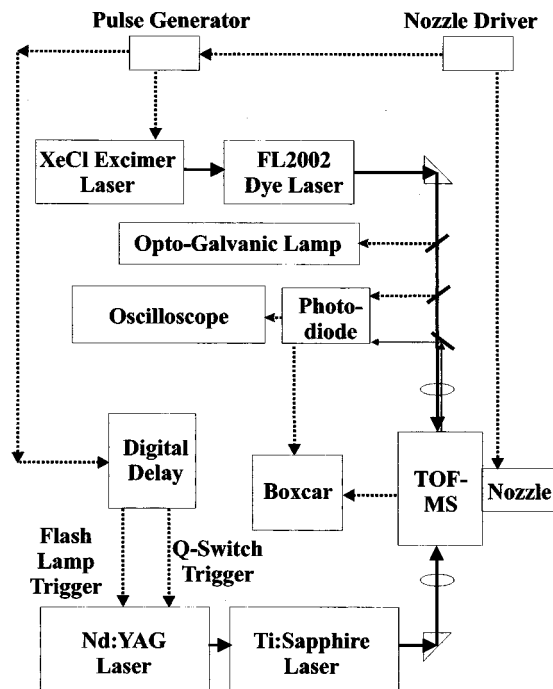


FIG. 2. The experimental arrangement.

branches,  $P$ ,  $P_Q$ ,  $R_Q$ , and  $R$ . The  $Q$ -branch is, of course, absent and the resultant gap formed a convenient means of calibrating the Ti:sapphire laser output. In the present experiment, the  $P$ -branch lines were used exclusively to pump the even  $J$  levels of the  $b(^1\Sigma_g^+)$  state, labeled  $J_b$  in the subsequent discussion. Odd levels are forbidden because of the zero spin of the <sup>16</sup>O nucleus.

The even rotational levels with  $J_b=0-16$ , pumped in this way, were probed by (2+1) REMPI *via*  $v=3$  of the  $d(^1\Pi_g)$  Rydberg state. The spectra are shown in Figs. 3 and 4. All of the peaks which appear in the spectra recorded *via*  $J_b=0-8$ , shown in Fig. 3 can be assigned by two-photon selection rules in which, for a  $\Omega(1 \leftarrow 0)$  transition,  $O$ -,  $P$ -,  $Q$ -,  $R$ -, and  $S$ -branches are all allowed but above  $J=3$  the  $Q$ -branch has no significant intensity relative to the other branches.<sup>8</sup>

The spectrum recorded *via*  $J_b=0$  consists of a single peak which is due to an  $S$ -line, while in that recorded *via*  $J_b=2$ , there are three strong peaks arising from  $P$ -,  $R$ - and  $S$ -lines. Those spectra recorded *via*  $J_b=4-8$  have clearly resolved  $O$ -,  $P$ -,  $R$ -, and  $S$ -lines (the  $Q$ -lines are essentially absent). In the spectrum recorded *via*  $J_b=10$ , shown in Fig. 4, the  $S$ -line is significantly weaker than the  $O$ -,  $P$ -, and  $R$ -lines, even allowing for the relatively large uncertainties in the peak intensities. In addition, two extra, weak lines, labeled  $R_2$  and  $S_2$ , are observed *ca.* 150 cm<sup>-1</sup> above the  $S$ -line. In the spectrum recorded *via*  $J_b=12$ , both  $R$ - and  $S$ -lines are weak and strong  $R_2$ - and  $S_2$ -lines are observed. In the spectrum recorded *via*  $J_b=14$ , the higher-energy system contains  $O_2$ -,  $P_2$ -,  $R_2$ -, and  $S_2$ -lines, while essentially only the  $O$ -line of the original, low-energy system remains. Finally, in the spectrum recorded *via*  $J_b=16$ , the highest  $J_b$  level that it was possible to pump, only the four branches of



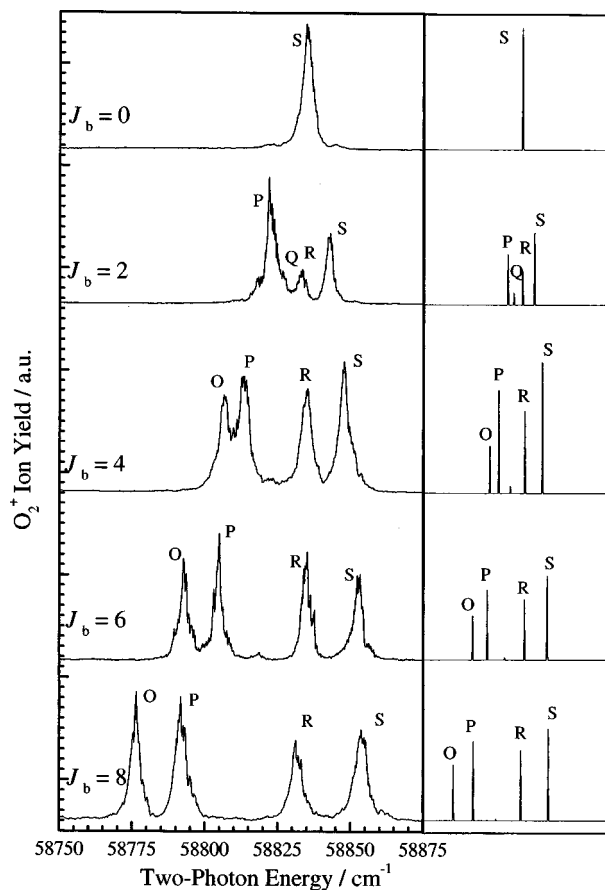


FIG. 3. The (2+1) REMPI spectrum of  $v=3$  of the  $d(^1\Pi_g)$  Rydberg state, excited from various rotational levels,  $J_b$ , of  $v=0$  of the  $b(^1\Sigma_g^+)$  state, in which essentially unperturbed rotational levels of the Rydberg state are accessed. The panels on the right show the relative Hönl-London factors for the various branches as stick diagrams in which the intensity of each calculated S-branch is put equal to the observed S-branch.

the high-energy system are observed, of which, the  $J'=17(R_2)$  appears as a doublet.

The transition energies of the observed rotational lines are presented in Table I. Term values of the rotational levels of  $v=3$  of the  $d(^1\Pi_g)$  Rydberg state, calculated using the present experimental data together with the known molecular constants of the  $b(^1\Sigma_g^+)$  state,<sup>9</sup> are presented in Table II. Most rotational levels are observed *via* two transitions and the quoted values are an average of the two values calculated from these transitions and are consistent to  $\pm 1$   $\text{cm}^{-1}$ . The increase in the error, relative to that of the calibration procedure alone, is due to the uncertainty in locating the line maxima.

There are no systematic variations with  $J'$  in the observed line widths, which are  $3.5 \pm 1$   $\text{cm}^{-1}$ . The only exceptions are the two components of the  $J'=17(R_2)$  doublet which are significantly narrower with line widths of around 2  $\text{cm}^{-1}$ .

#### IV. DISCUSSION

The  $3s(^1,^3\Pi_g)$  Rydberg states are known to couple both to each other and to several valence states.<sup>1-6,10,11</sup> The potential energy curves of the states involved are illustrated in

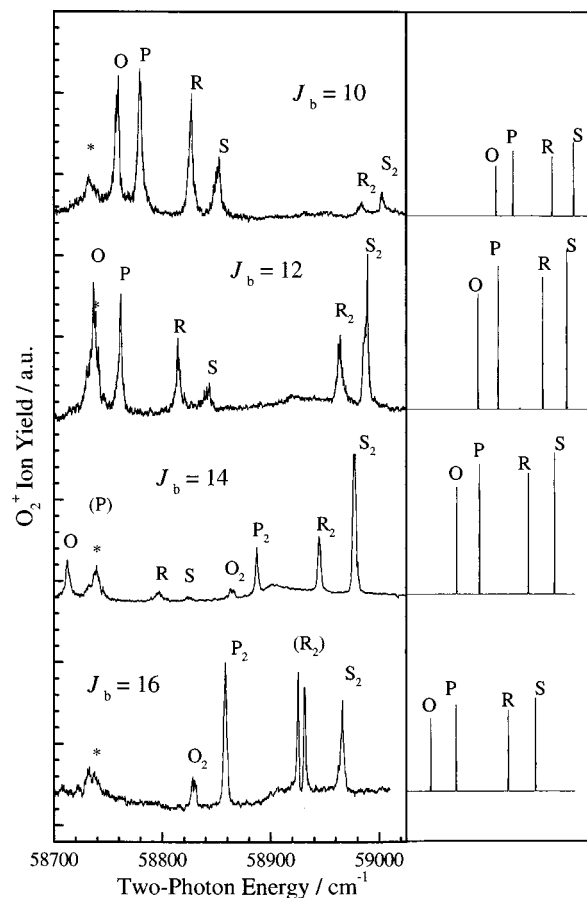


FIG. 4. The (2+1) REMPI spectrum of  $v=3$  of the  $d(^1\Pi_g)$  Rydberg state, excited from various rotational levels,  $J_b$ , of  $v=0$  of the  $b(^1\Sigma_g^+)$  state, in which perturbed rotational levels of the Rydberg state are accessed. The panels on the right show the relative Hönl-London factors for the various branches as stick diagrams in which the intensity of each calculated S-branch is put equal to the sum of the observed S- and  $S_2$ -branches. The starred band is due to a (3+1) signal from ground state  $\text{O}_2$ .

Fig. 1. It has proved to be extremely difficult to gain an in-depth understanding of the Rydberg-valence interactions, partly because of the complexity of the system but largely because of the uncertainties in the experimentally derived

TABLE I. Energies, in  $\text{cm}^{-1}$ , of the observed rovibronic transitions in the (2+1) REMPI spectrum of  $v=3$  of the  $d(^1\Pi_g)$  Rydberg state, excited from various rotational levels,  $J_b$ , of  $v=0$  of the  $b(^1\Sigma_g^+)$  state.

$J_b$	O	P	R	S
0				58 834.7
2		58 821.9	58 833.3	58 842.9
4	58 806.5	58 813.5	58 835.2	58 847.7
6	58 792.6	58 805.0	58 835.1	58 853.3
8	58 776.6	58 791.7	58 831.2	58 853.7
10	58 759.5	58 779.3	58 827.1	58 852.7
12	58 737.1	58 762.5	58 815.1	58 844.2
14	58 712.5	58 739.4	58 797.4	58 823.1
$J_b$	$\text{O}_2$	$\text{P}_2$	$\text{R}_2$	$\text{S}_2$
10			58 983.9	59 003.1
12			58 965.1	58 989.9
14	58 863.3	58 887.3	58 944.5	58 977.6
16	58 828.0	58 857.9	58 925.2/58 931.0	58 966.0

TABLE II. Term values of  $v=3$  of the  $d(^1\Pi_g)$  Rydberg state obtained using transitions observed in the present work and the known molecular constants of the  $b(^1\Sigma_g^+)$  state (Ref. 9). The calculated values are generated by constants given in Ref. 6.

$J'_1$	Term value/cm <sup>-1</sup>	Calculated/cm <sup>-1</sup>	$J'_2$	Term value/cm <sup>-1</sup>
0		71 950.0		
1	71 952.4	71 952.4		
2	71 956.7	71 957.3		
3	71 963.6	71 964.4		
4	71 973.3	71 974.0		
5	71 985.4	71 985.9		
6	71 998.5	72 000.0		
7	72 014.9	72 016.3		
8	72 034.3	72 034.7		
9	72 054.0	72 055.0		
10	72 076.2	72 077.3		
11	72 102.0	72 101.4	11	72 259.1
12	72 127.3	72 127.0	12	72 278.0
13	72 154.2	72 154.2	13	72 303.0
14	72 183.4	72 182.7	14	72 328.8
15	72 211.8	72 212.4	15	72 358.7
16	72 237.5		16	72 387.3
			17	72 425/72 431
			18	72 466.6

transition energies and line widths. However, in work published recently, Lewis *et al.*<sup>5,6</sup> presented a coupled Schrödinger equation (CSE) approach to the problem which utilized a number of sources of experimental data to provide the best insight to date into the perturbations of these states. In particular, the effect of the interaction of individual bound vibrational levels of the  $II(^1\Pi_g)$  valence state with the rotational manifolds of the  $v=1-3$  levels of the  $d(^1\Pi_g)$  Rydberg state were discussed in great detail.

In the CSE approach, the input to the coupled equations are the transition moments to the  $d(^1\Pi_g)$  Rydberg and the  $II(^1\Pi_g)$  valence states, their diabatic potentials and the coupling strength between the two states. According to the calculations of Lewis *et al.*,<sup>5,6</sup> the observed perturbations are predominantly due to valence levels which lie higher in energy than the Rydberg levels which they perturb. However, two factors mean that transitions to the unperturbed levels of this valence state are not seen directly. First, it was proposed that there is a low ionization efficiency from the  $II(^1\Pi_g)$  valence state because (i) it has a very different equilibrium geometry ( $R_e=1.49$  Å) from that of the ground state of the ion ( $R_e=1.14$  Å), resulting in a poor Franck-Condon overlap between the two, (ii) it has a large predissociation rate resulting from a coupling with the  $I(^1\Pi_g)$  repulsive valence state, and (iii) the ionization step is a two-electron process to the ground state of the molecular ion which is the only state accessible at the energy of the probe photon. Second, it was proposed that the two-photon transition moment  $II(^1\Pi_g) \leftarrow \leftarrow a(^1\Delta_g)$  is negligibly small relative to that to the Rydberg state. In the discussion below, we retain this assumption for the  $II(^1\Pi_g) \leftarrow \leftarrow b(^1\Sigma_g^+)$  transition, both the  $a(^1\Delta_g)$  and  $b(^1\Sigma_g^+)$  states having the same configuration.

While the  $II(^1\Pi_g)$  valence state levels are not observed directly, their positions have been predicted from the perturbational effects that they have on the Rydberg state. Thus, it

was proposed that the  $v=8$  and 9 levels of the  $II(^1\Pi_g)$  valence state perturb  $v=2$  of the  $d(^1\Pi_g)$  state while  $v=13, 14$ , and 15 perturb the  $v=3$  level. The result is that two levels are coupled at each  $J$ , the lower of which is predominantly Rydberg in character while the higher has predominantly valence character. Since only the Rydberg state can be detected because of its greater ionization efficiency, only the rotational levels of the lower of the two coupled vibronic levels are observed when  $J'$  is low, between 1 and 10, as can be seen in Fig. 3. As  $J'$  increases, the rovibronic levels of the Rydberg state become close to being isoenergetic with those of the valence state as a result of the difference in the  $B$  values of the two states. When the rovibronic levels become nearly isoenergetic, the two coupled states have almost equal contributions from both diabatic states, and both become detectable through the Rydberg component. Figure 4 shows that this situation holds true for  $J'=11-15$ . Further increase in  $J'$  results in the rovibronic levels of the Rydberg state becoming higher in energy than those of the valence state and therefore only rotational levels of the higher of the coupled pairs of vibronic levels are detected as shown for  $J'=16-18$ .

Lewis *et al.*<sup>6</sup> reported that the experimental term values for  $J' \leq 15$  could be reproduced by the spectroscopic constants  $v_0=71\,950$  cm<sup>-1</sup>,  $B=1.211$  cm<sup>-1</sup>, and  $D=4.9 \times 10^{-4}$  cm<sup>-1</sup> which were consistent with a single value for  $B$  of 1.15 cm<sup>-1</sup> reported by Sur *et al.*<sup>3</sup> from assignments for  $J' \leq 8$ . The term values generated by these constants are presented in Table II and agree well ( $\pm 1.5$  cm<sup>-1</sup>) with the present experimental values. While the rotational line positions are in excellent agreement with those generated by the model of Lewis *et al.*,<sup>6</sup> the line widths observed in the present experiment do not agree with those predicted by the model. In addition, the relative intensities of the lines observed in the spectra appear to differ from those predicted by the two-photon transition strength expressions.<sup>8</sup>

The CSE calculation<sup>6</sup> was performed with predicted lifetimes for the Rydberg and bound valence states that correspond to line widths of 0.75 and 8 cm<sup>-1</sup>, respectively. The lines produced in the simulation were then convoluted with a Gaussian instrumental function of 3 cm<sup>-1</sup> in order to reproduce the 4 cm<sup>-1</sup> line widths observed by Ogorzalek-Loo.<sup>2</sup> This value is in good agreement with the line widths observed in the present experiment which are, with one exception,  $3.5 \pm 1$  cm<sup>-1</sup>. The exception is the doublet observed for the  $J'=17$  level which has observed line widths of  $\leq 2$  cm<sup>-1</sup>. This places an upper limit on any experimental broadening of the lines and means that the widths of the rotational lines of the Rydberg state which do not undergo strong rotational interaction with the bound valence state, i.e.,  $J'=1-10$  are appreciably greater than 0.75 cm<sup>-1</sup>. Furthermore, as the maximum of the rotational perturbation near  $J'=13$  is approached, it was predicted that the increased mixing of the Rydberg and valence levels would produce a rapid broadening of the Rydberg levels. If, as it appears, there is no appreciable broadening of the most perturbed levels,  $J'=11-15$ , it follows that the line widths of the unperturbed valence state levels are not appreciably greater than 4 cm<sup>-1</sup>, in contrast to the predicted width of 8 cm<sup>-1</sup>. The fact

that there is no rotationally dependent broadening implies that the line widths of the Rydberg and valence states before they couple to each other are not significantly different. However, the observed line widths of ca.  $4\text{ cm}^{-1}$  must mean that both states are predissociated to a small extent.

The possible effect of resonances in the ionization step on line intensities in any REMPI experiment should also be considered. In the present experiments where  $v=3$  of the  $d(^1\Pi_g)$  state is excited from  $v=0$  of the  $b(^1\Sigma_g^+)$  state, the third, ionizing photon from the probe laser accesses the energy range  $101\,340\text{--}101\,950\text{ cm}^{-1}$ . In wavelength terms this corresponds to a range of  $98.68\text{--}98.09\text{ nm}$  and spans the region of a one-photon transition from  $v=0$  of the ground state to  $v=2$  of a  $3s$  Rydberg state based on the  $a^4\Pi_u$  ionic core.<sup>12</sup> The vibrational level lies above the lowest ionization energy and is observed as a result of autoionization. In the experiments of Ogorzalek-Loo *et al.*,<sup>1</sup> where  $v=3$  of the  $d(^1\Pi_g)$  state is excited from  $v=0$  of the  $a(^1\Delta_g)$  state, the ionizing photon does not access an energy region in which a vibrational level of the autoionizing Rydberg state has been observed. There appears to be no significant difference in the widths and relative intensities of lines which terminate on a common upper rotational level of the  $d(^1\Pi_g)$  state in the two two-photon spectra, in one of which the ionizing photon is in resonance with a vibrational level of the autoionizing Rydberg state but is off resonance in the other. We conclude that any effects of resonances at the three-photon level are minor and will subsequently be ignored.

As there is no significant variation in the observed line widths, nor is saturation a problem, the peak heights can be used as a monitor of intensity. The intensities of the peaks in the spectra shown in Fig. 3 which are due to transitions to rotational levels of the  $d(^1\Pi_g)$  Rydberg state which do not undergo strong coupling to the  $H(^1\Pi_g)$  valence state should obey the two-photon transition strength expressions.<sup>8</sup> The predicted intensities, normalized to that of the observed  $S$ -branch line, are illustrated as stick diagrams in the panel on the right of Fig. 3. While there are quite large uncertainties in the observed intensities of up to  $\pm 15\%$ , there does appear to be a general trend where, as  $J'$  increases, the observed line strengths become progressively less than predicted.

In the region of strongest rotational perturbation, the predicted intensities, normalized to that of the observed  $S+S_2$ -branch line, are illustrated as stick diagrams in the panel on the right of Fig. 4. As before, the differences between the observed and calculated intensities are outside the experimental uncertainties. The overall trend is that, as the degree of perturbation that a rotational level undergoes increases, the intensity with which it is observed decreases.

This effect can be explained by a simple two-state coupling model. The coupling involves two electronic states of very different electronic character, one Rydberg and one valence, and our explanation will center on the relative ionization efficiencies of these two states at the probe wavelengths used. We will find that  $J$ -dependent predissociation, for which there is no evidence from the essentially constant line widths, need not be invoked.

The wave functions for a pair of coupled rovibronic levels can be written

$$\begin{aligned} |d_1\rangle &= c_{1,J}|e_1v_1\rangle + c_{2,J}|e_2v_2\rangle, \\ |d_2\rangle &= c_{2,J}|e_1v_1\rangle - c_{1,J}|e_2v_2\rangle, \end{aligned} \quad (1)$$

where a diabatic basis  $|e_i v_i\rangle \equiv |e_i\rangle|v_i\rangle$  has been adopted, and the subscript 1 on the right-hand side refers to the electronic and vibrational level of the pure Rydberg state (Ry) to which the valence state ( $e_2 \equiv V$ ) is coupled. The coefficients of mixing must satisfy  $c_{1,J}^2 + c_{2,J}^2 = 1$  and are  $J$ -dependent through the energy difference between the diabatic states,  $\Delta T_e + E(v_{1,J}) - E(v_{2,J})$ , which depends on  $J$  because of the large difference in rotational constants  $B_1$  and  $B_2$ , an aspect which has been fully explored by Lewis *et al.*<sup>6</sup> The valence state that is coupled to the  $d(^1\Pi_g)$  state seems to be spectroscopically inaccessible. This can arise from two causes: (i) the Franck-Condon factor  $\langle v_2|v_b\rangle$  is much smaller than that for reaching the Rydberg state  $\langle v_1|v_b\rangle$  because of the much larger  $R_e$  value of the valence state, and (ii) the oscillator strength from the initial  $b(^1\Sigma_g^+)$  state may be predominantly carried by the Rydberg component. The two-photon absorption cross sections for accessing the two mixed states  $d_1$  and  $d_2$  defined by Eq. (1) are

$$\sigma_{i \leftarrow b}^{(2)} \propto c_i^2 \langle v_1|v_b\rangle^2 (\mu_{\text{Ry};b}^{(2)})^2, \quad (2)$$

where, in the present case, the two-photon electronic transition dipole  $\mu_{\text{Ry};b}^{(2)}$  is required and we have implicitly summed over all virtual states. If the ionizing photon energy is only sufficient to leave the ion in low vibrational levels,  $v^+$ , of its lowest electronic state, the cross section for ionization of the first of the two mixed Ry/ $V$  states,  $d_1$ , is

$$\sigma_1^{\text{ion}} \propto [c_1 \langle v^+|v_1\rangle \mu_{E,\text{Ry}} + c_2 \langle v^+|v_2\rangle \mu_{E,V}]^2, \quad (3)$$

and the cross section for ionizing the other vibronically mixed component,  $d_2$ , is obtained by reversing the coefficients  $c_1$  and  $c_2$  as can be seen from Eq. (1). The arrangement of potential energy curves which support the two diabatic vibrational wave functions  $|v_1\rangle$  and  $|v_2\rangle$  is such that only the Rydberg state has good Franck-Condon overlap with low vibrational levels of the ion as was the case in the  $d \leftarrow b$  excitation step. The second Franck-Condon factor in Eq. (3) can thus be neglected. This selective ionization *via* the Rydberg component is further enhanced as has been suggested if the electronic transition required for ionization of the valence component,  $\mu_{E,V}$  in Eq. (3), requires a core configuration rearrangement in order to achieve the ground state of the ion.

To model the cross section for the overall ionization process  $X^+ \leftarrow d_1/d_2 \leftarrow b$ , we neglect the second term in Eq. (3), and multiply the cross sections for the pump and ionizing steps to obtain the relative intensities of lines in a REMPI spectrum. The result, depending on which of the two intermediate states  $d_1$  or  $d_2$  is resonant, is  $I_i \propto c_i^4$ . The summed REMPI signal from a given branch of the two components of a mixed vibronic state, e.g.,  $S_1(J') + S_2(J')$ , is thus  $\propto c_{1,J}^4 + c_{2,J}^4$ . Since  $c_1^2 + c_2^2 = 1$ , we see that when the mixing is at its maximum, ( $c_{1,J}^2 = c_{2,J}^2 = 0.5$ ),  $c_{1,J}^4 + c_{2,J}^4$ , and hence the summed REMPI signal  $I_1 + I_2$ , is at its minimum, falling to half of that from the corresponding branch of a pure Rydberg state. This is in line with the reduction in intensity of the most heavily mixed rotational branches. For example, in the

spectrum recorded *via*  $J_b=10$  shown in Fig. 4, the intensity summed over the two  $S$ -branches that terminate in  $J'=12$ ,  $S_1(J)$  and  $S_2(J)$ , is approximately one-half of the intensity of the neighboring  $P$ -branch for which  $J'$  is not strongly mixed. On closer inspection none of the rotational band intensities follow the Hönl–London factors closely, and the extent of the loss in intensity is well correlated with the difference in rovibronic term values of the Rydberg and nearest valence levels. Thus, the lines become weaker as  $J'$  increases from 1 to 10 and nears the region of greatest interaction at  $J'=12$ –14, and become stronger again between  $J'=16$  and 18.

In the study of Lewis *et al.*,<sup>6</sup> predissociation of the levels of the bound valence state by a repulsive valence state, the cause of the proposed large line widths, was cited as one of the factors in the poor ionization efficiency from the unperturbed valence state levels and hence its nonappearance in the REMPI spectra. Indeed, the predicted line width was used as one of the most important criteria in optimizing the comparison between the observed and calculated REMPI spectra. The effect of this approach is that the calculated two-photon transition intensity of any Rydberg rotational level which is perturbed by a valence rotational level is spread over a certain wave number range but is still included in the simulation. However, the current results suggest that the predissociation of the valence state is not appreciably greater than that of the Rydberg state and hence does not make a significant contribution to the decrease in the ionization efficiency of the valence state relative to that of the Rydberg state. Rather, the major factor in lowering the ionization efficiency of the valence state is a poor Franck–Condon overlap with the ground state of the ion and the necessity of a change in the core state. Thus, a different effect of the coupling is suggested in which the calculated two-photon transition intensity of any Rydberg rotational level which is perturbed by a valence rotational level is decreased in the REMPI spectrum rather than being redistributed.

The two models predict a different variation in REMPI intensities of lines in regions of rotational perturbation and this will be particularly evident when these lines overlap, e.g., in a turning point of a particular branch. In their simulations of the (1,0), (2,0), and (3,0) bands, Lewis *et al.*<sup>6</sup> noted only two experimental features which their model could not accurately reproduce. The simulation of the (1,0) spectrum contained too much intensity in two narrow energy regions comprised mainly of turning points of the  $O$ - and  $P$ -branches including  $J' \leq 20$ . The rotational perturbation of this band is centered on  $J'=12$  and, for the reasons described, above their simulation may include too much intensity in this region.

It can be seen from the splitting of the  $J'=17$  level, observed in Fig. 4, that there is a further local perturbation involving the upper of the two coupled vibronic states. This feature was also noted by Lewis *et al.*<sup>6</sup> from less well resolved spectra.<sup>2</sup> They postulated that the much weaker perturbation experienced by this level was due to the weak rotational interaction with the  $II(^1\Delta_g)$   $v=6$ ,  $J=17$  rovibronic level. The characteristics of our spectra are consistent with

this conclusion and the splitting of the feature (ca.  $6\text{ cm}^{-1}$ ) is similar to that estimated from the reported spectra.<sup>2</sup> The narrower line widths of this doublet ( $2\text{ cm}^{-1}$ ) imply that the  $II(^1\Delta_g)$  state is predissociated to a lesser extent than both the  $d(^1\Pi_g)$  and  $II(^1\Pi_g)$  states which we now propose are predissociated to a very similar extent. This three-state coupling possibly results in an increase in the detection efficiency, because of the longer lifetime of the  $II(^1\Delta_g)$  state, as judged by the sum of the integrated intensities of the two doublet components relative to those of the other branch lines shown in the spectrum recorded *via*  $J_b=16$ , shown in Fig. 4. A similar interaction may cause the anomalously intense peak in the region of the  $P$ -branch of the spectrum recorded *via*  $J_b=2$ , shown in Fig. 3.

## V. CONCLUSION

The perturbed  $v=3$  level of the  $d(^1\Pi_g)$  Rydberg state of O<sub>2</sub> has been excited from the ground state in an OODR experiment *via*  $J=0$ –16 of  $v=0$  of the  $b(^1\Sigma_g^+)$  state. Line positions compare well with those from a vibronic coupling calculation by Lewis *et al.*<sup>6</sup> involving the valence  $II(^1\Pi_g)$  state. However, in contrast to theoretical predictions, no variation in the line widths is observed, with transitions to uncoupled rotational levels having essentially the same width as those to strongly coupled levels. Furthermore, line intensities in the REMPI spectrum do not follow the two-photon Hönl–London factors for the  $d \leftarrow b$  transition, branches involving the more strongly coupled levels being markedly weaker than expected. We attribute this to the lowered ionization cross section of the coupled valence/Rydberg states compared with the pure Rydberg state. It is characteristic of this model that a reduced REMPI signal will be seen even when the intensity arising from both coupled components is summed over.

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